

**OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY
AIR QUALITY DIVISION**

MEMORANDUM: October 13, 2016

TO: The Files

THROUGH: *HMS* Heather Sessing, Environmental Programs Specialist
Enforcement Section

THROUGH: *SA* Peer Review

FROM: *DSS* David Schutz, P.E.
New Source Permits Section

SUBJECT: Observation of Performance Tests
Permit 2004-302-TVR (M-2)
Continental Carbon Corporation
Carbon Black Production Facility (FAC ID 333)
Section 10, T25N, R2E
Ponca City, Kay County, Oklahoma
Located 1 mile south of the Intersection of US-60 and US-177
Test ID No. (TO-1): 9036

INTRODUCTION

On October 11 - 12, 2016, performance tests were observed at the Continental Carbon facility at Ponca City. Testing was to determine compliance with emissions limitations of Permit No. 2004-302-TVR (M-2) for three thermal oxidizers. Present for the testing were Mr. David Schutz of AQD; and Mr. Todd Miller and Ms. Pamela Alexander of Continental Carbon.

Testing was successfully commenced on October 11, 2016. Preliminary results show NO_x, CO, VOC, and SO₂ emissions well within permit limits.

PROCESS DESCRIPTION

Feedstock oil from crude oil refineries is received by tank truck, tank cars, and pipeline into a 65,000-barrel insulated cone roof tank. Fresh oil, received by pipeline from the nearby ConocoPhillips refinery or other delivery, is blended with the oil in inventory upon receipt. Material from this tank is circulated through a heater and returned to the tank through an internal mixing nozzle which provides for uniform feed quality.

The oil is pumped to the reactors by way of an in-line oil pre-heater exchanger. From the outlet of the oil pre-heater, the oil flows into the reactor, where the oil is partially combusted at about 2,800°F. Combustion air is provided by electric motor-driven forced-draft blowers. This air passes through an in-line air pre-heater (similar to the oil charge) except that the combustion air is on the shell side and hot quenched reactor product gases are on the tube side. Natural gas or feedstock oil is used to maintain the reactor temperature.

During this incomplete or partial combustion, potassium carbonate (K_2CO_3) is injected at the reactor face plate in parts per million quantities as a product structure control additive. Also during this process, carbon black and other products of incomplete combustion, including reduced sulfur compounds, are formed.

The carbon-laden gases from the reactor are cooled to about 1,000-1,500°F by water quenching in the "quench" section of the reactor. These quenched flue gases then pass through the "residence section" and then into the oil- and air-pre-heaters, as previously described. The partially cooled flue gases (500°F) then go through the main bag filters (MBFs) for carbon black recovery. No carbon black production occurs during warm-up or emergencies when there is no oil in the reactor, hence the combustion gases are not carbon black-laden, nor do the gases have significant concentrations of VOC, CO, H_2S , CS_2 , HCN, SO_2 and COS at these times.

While in production, about 20 percent of the filtered gases from the MBFs go to the waste gas combustor (WGC) and then to the rotary dryers for drying the pelletized carbon black. The surplus waste gas (about 80 percent of the total reactor wasted gas) not used in the waste gas combustors has in the past been vented directly to the atmosphere. Continental Carbon now burns these waste gases in the new thermal oxidizers.

The filtered waste gas has a BTU content of about 60-80 BTU/SCF. While low in BTU content, this gas is easily combusted without supplemental fuel. The combustion efficiency in the waste gas combustors is approximately 98.0 percent. The combustion/dryer system on each unit uses the waste gases from its respective MBFs as the primary source of fuel.

The surplus waste gases go to the thermal oxidizers. The combustion zone temperature for the thermal oxidizers will range from 1,500°F to 2,100°F, depending on the specific product being made. The carbon black is collected in the MBFs. Particulate matter from process equipment that is part of the dust management system is collected in the cleanup bag filter (CUBF). The collected material from the CUBF is ultimately discharged to the pneumatic conveyor.

The carbon black then enters a stage called the "Wet Process," where the loose, fine carbon black is consolidated into pellets. Carbon black collected in the main bag filter (MBF), exhaust bag filter (EBF) and in the clean-up bag filter (CUBF), flows through a pulverizer into the accumulator tank and then into the pelletizer, where the carbon black is mixed with an equal weight of water and wetting agents and formed into small pellets. These wet pellets drop through a chute into one end of a rotary drying drum.

Approximately 20 percent of the filtered reactor waste gases exiting the MBFs are combusted in the waste gas combustors. The combusted gases go around the outside of the rotating drying drum, then through the inside of the rotating drum, countercurrent to the carbon black flow. The gases, plus water vapor from the dried pellets and any airborne particulate matter due to carbon black movement, then go to the exhaust bag filter (EBF). The EBF efficiency is 99.9 percent for particulates. Gases filtered by the EBF exit to the atmosphere via their respective thermal oxidizers. The thermal oxidizers release the unneeded combusted heating gases from the unit drying drums to the atmosphere. The combustion efficiency of the waste gas combustors, integral to the drum dryers, is approximately 98.0 percent.

The dried carbon black pellets leaving the dryer drum are lifted by a bucket elevator system to the top of closed storage tanks. Pellets are discharged from the bucket elevator across screen separators. These separators discharge the product carbon black pellets into closed screw systems, leading into the storage tanks.

The carbon black storage tanks are vented through a single sock fabric particulate filter. Fugitive dust due to product movement is controlled by a vacuum cleanup system that exhausts through the CUBF. Carbon black is gravity-loaded from the storage tanks into hopper cars, specialty bulk containers for bulk or semi-bulk shipments, or is bagged by existing valve bag packers for shipment in boxcars or trailers.

Carbon black production capacity for each unit is listed for determining percent of capacity during testing:

Unit No.	Limits (million lb/yr)
1	80
2	100
3	80
4	100
Total	360

Unit No. 2 produces "carcass" black, while the other units produce "tread" black.

PERFORMANCE TESTING METHODS

Emissions of criteria pollutants were tested by the following EPA reference methods.

- Method 1: sample and velocity traverses
- Method 2: stack gas velocity and volumetric flow rate
- Method 3A: gas analysis for carbon dioxide, oxygen, and dry molecular weight
- Method 4: moisture content in stack gases
- Method 5: PM emissions from stationary sources
- Method 6C: SO₂ emissions from stationary sources
- Method 7E: NO_x emissions from stationary sources

- Method 10: CO emissions from stationary sources
- Method 25A: VOC emissions from stationary sources
- Method 202: condensable PM

Particulate testing used a water-cooled probe. A Method 5 sampling train incorporates Method 2 for stack velocity and Method 4 for moisture content. A sample line may be attached to the discharge from the sample train to collect dry gas for Method 3A gas analysis that determines the concentrations of CO₂, nitrogen, and oxygen. The sampling train is to consist of at least four impingers in an icewater bath (one empty, two with measured volumes of distilled water, and the fourth with silica gel).

Methods 6C and 7E are instrumental methods for determining concentrations of SO₂ and NO_x, respectively. Meters must be calibrated after each run. Before and after sampling, a system bias check is conducted instead of a leak check. The maximum allowable bias is 5%; the NO_x bias was shown as 0.83% prior to commencing testing. Concentrations are recorded on a computer. The minimum sampling time for each method is "twice the system response time". The system response time was stated as 2.25 minutes. Sampling was conducted for 72 minutes per run. Concentrations of SO₂ and NO_x are used in conjunction with Methods 2 and 4 to yield mass emissions rates. A glass wool filter is necessary to remove ammonia, fluorides, and water-soluble cations. The system must be shown to have a properly-working NO_x→NO₂ converter, demonstrated by a 30 minute converter test with at least a 90.0% conversion efficiency; the converter efficiency was 97.3%. Calibration gases were labeled "EPA Protocol 1."

Method 10 for CO uses non-dispersive infrared testing. The sample line is required to be leak-free, but specific methods for verifying this are not stated. The system bias checks suffice to verify that the sample line is secure. Calibration gases were labeled "EPA Protocol 1."

Method 25A is an instrumental method which uses a flame ionization analyzer to measure hydrocarbon concentrations. The method is applicable to alkanes, alkenes, and aromatics; organic emissions from the facility are among these classes. VOCs are reported in terms of the calibration gas. Propane was used as the calibration gas. Method 25A testing is applicable to both combustion and non-combustion types of air pollution controls. A leak check is not required for Method 25A, and a probe filter is optional. Since flame ionization measures a signal produced by reaction of carbon with oxygen, there is lower response for measurement of compounds which already include oxygen, including formaldehyde, methanol, and phenol.

Method 202 is now referred to as the "dry impinger method" for determining condensable PM. A gas stream is first filtered using a conventional Method 5 train. The gas from the Method 5 filter is first cooled then passed through two empty impingers allowing fall-out of condensed PM. There is a filter following the two initially-empty impingers which is maintained at 85°F or less. There are two impingers following the filter, one with distilled water and one with silica gel; these last two are part of the moisture determination. The filters and impinger catches are extracted with hexane to remove condensed organic matter from inorganic matter.

Tests were conducted by METCO of Dallas, TX, by a team led by Mr. Jason LaCroix.

Cal Gas Specifications

Gas	Cal Range	Concentration	Cylinder Serial No.	Expiration Date
O ₂	Mid	10.97%	EB0046694	6/27/24
	High	20.3%	ALM034206	4/15/23
CO ₂	Mid	10.97%	EB0046694	6/27/24
	High	20.1%	ALM034206	4/15/23
VOC (as propane)	Low	27.00 ppm	CC106323	7/11/23
	Mid	47.8 ppm	CC66989	11/4/22
	High	85.5 ppm	BLM004013	5/22/23
CO	Low	45.4 ppm	EB0049161	10/04/23
	Mid	466 ppm	ET0005657	12/19/23
	High	957 ppm	LL34020	4/16/23
NO _x	Low	50.6 ppm	ALM034254	9/29/18
	Mid	471 ppm	EB0018519	12/19/23
	High	943 ppm	LL62500	12/05/21
SO ₂	Mid	976 ppm	ET0004473	4/17/24
	High	2330 ppm	BAL3904	12/10/21

UNIT 1 AND 2 THERMAL OXIDIZER

The unit was at a stable production level approaching the unit capacity (the operator requested the rate be held confidential).

The stack for the TO was approximately 138 feet in height, 130 inches in diameter, with sampling ports located 71 feet downstream from the nearest flow disturbance and 13 feet upstream from the opening of the stack. The diameter ratio for Method 1 is 6554 : 1.20. This diameter ratio is required by Method 1 to utilize at least 16 sampling points, 8 on each of two perpendicular diameters. Sampling was conducted at 24 points, exceeding the minimum as required by Method 1.

The stack was climbed and testing procedures were observed. The PM sampling trains were assembled as required by Methods 5 and 202. A second heat-traced line was used for gas-phase pollutants. No sources of bias were noted from the testing equipment. Testing technique met the requirements of the methods.

Testing was interrupted by a lighting storm on October 11; it was completed on October 12, 2016. Preliminary test data showed the following information.

Parameter	Required Range	Test Run #1
Carbon Black Production, lb/hr	≥ 90%	NA
TO Operating Temperature, °F	≥ 1,500	1,917
Stack Velocity, ft/sec	--	46
Stack Flow, ACFM	--	253,109
Stack Flow, SCFM	--	44,018
Stack Moisture Content	--	33.03%
M4 Stack Sampling Volume, ft ³	≥ 21	NA
Stack Sampling Points	≥ 16	24
Stack Cyclonic Flow Angle, deg.	< 20°	1°
Sampling Time, minutes	≥ 60	72
Stack Temperature, °F	--	1,518
Stack O ₂	--	5.35%
Stack CO ₂	--	8.63%
Post-Test Leak Check, cfm	< 0.2	NA
Isokinetic Variation	100±10%	NA
NO _x , ppm at Stack	--	285
NO _x , lb/hr	< 270	91.1
CO, ppm at Stack	--	0.4
CO, lb/hr	< 475	0.08
VOC, ppm at Stack	--	1.07
VOC, lb/hr as C ₃ H ₈	≤ 17	0.33
SO ₂ , ppm at Stack	--	736
SO ₂ , lb/hr	≤ 2,568	327.4
PM, Filterable, lb/hr	---	NA
PM, Condensable, lb/hr	--	NA
Total PM, lb/hr	< 40.97	NA

NA = not yet available.

NO₂, was shown as 8 ppm.

SUMMARY

Performance testing observed was properly conducted. A written report of test results is anticipated within 30 days to document compliance with emissions limitations.